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Optical spectra of UV-irradiated rubidium and caesium nitrate crystals

V. Anan'ev*, M. Miklin, N. Nelyubina, M. Poroshina

Department of Analytical Chemistry, Kemerovo State University, Krasnaya 6, Kemerovo 650043, Russia

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Abstract

Absorption spectra of $RbNO_3$ and $CsNO_3$ nitrate single crystals have been studied. It is stated that the photo-induced absorption in UV-irradiated samples consists of three bands. Thermal annealing and photo-bleaching (>310 nm) of the bands have been investigated. It is found that two low-energy bands are due to peroxynitrite and the high-energy band is due to the complex $[NO_2^- \cdots O]$. The mechanism for the nitrite ion formation from the peroxynitrite ion and the complex has been proposed.

Keywords: Peroxynitrite; Nitrite; Exchange-coupled complex; Photolysis; Alkali nitrate crystals; Absorption spectra

1. Introduction

The photo-decomposition of alkali nitrate crystals has been studied for more than 70 years. The first two products of photo-decomposition that were identified [1,2] were nitrite and molecular oxygen. In 1983, it was stated that the aqueous solution of the UV-irradiated solid KNO_3 contains peroxynitrite and its concentration correlates with the intensity of the UV-induced absorption [3]. The role of peroxynitrite in the processes taking place during the photolysis of solid nitrates and after it was studied independently by several teams of researchers [3–11].

The mechanism for the photo-decomposition of crystalline alkali nitrates was theoretically grounded on the basis of analysis of the symmetry, multiplicity and energy of electronic states of the nitrate ion and product [5]. The formation of nitrite and peroxynitrite via independent pathways, taking into consideration different kinetics of their photo-bleaching and thermal annealing determined by means of chemical analyses of UV-irradiated KNO_3 crystals, was postulated in [4,6]. According to this mechanism, nitrite and peroxynitrite were to be formed from different excited states of the nitrate ion—a triplet and a singlet, respectively, in conformity with the Vigner Rule. This result seems ambiguous because triplet excited states of the peroxynitrite ion must be formed under photolysis and their dissociation can result in the nitrite ion and oxygen.

That peroxynitrite is a precursor of nitrite under photolysis, was stated in [7] on the basis of the ESR data on the NO_2 formation during the radiolysis of pre-treated (UV irradiation and photo-bleaching) KNO_3 crystals. Besides, nitrite is formed from peroxynitrite during dissolving. On the one hand, there is no doubt about the formation of nitrite under UV irradiation in solid state, on the other hand, the quantitative interpretation of the experimental data is not evident because the yield of NO_2 in irradiated nitrate crystals depends very strongly on the competition between the nitrite ions and the nitrate ions [8].

Plumb and Edwards [9,11] share the point of view of [3,7], not excluding the possibility of the formation of a certain part of the nitrite ions not involving the peroxynitrite ions. It followed from the fact that the common method of determining the content of nitrite, involving the dissolving of the UV-irradiated nitrate samples when $pH = 7$, is not reliable [11] while the true nitrite accumulation is of a non-linear character [9]. Though their results are of great importance, the mechanism of solid alkali nitrate photo-decomposition proposed by the authors needs further experimental checking because they did not prove the possibility of the bleaching of peroxynitrite under UV irradiation at 253.7 nm and the formation of free atomic oxygen.

Thus, it can be stated that there is no mechanism for the photo-decomposition of crystalline alkali nitrates to account for all the experimental data available because

(i) all the assumptions concerning the processes in solid state have been made on the basis of the indirect data obtained after dissolving the irradiated samples;
(ii) the potentiometric titration method [12] used in [3,4, 6–11] to determine the peroxynitrite content for two to three repeated experiments had a great error [13];

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* Corresponding author. Tel.: +7-3842581940; fax: +7-3842581918.
E-mail address: eprlab@kemsu.ru (V. Anan'ev).

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(iii) all the experimental results have been obtained when studying the photolysis of solid potassium nitrate.

The goal of the present paper is to determine the mechanism for the nitrite ions formation in UV-irradiated crystalline alkali nitrates. This problem can be solved by means of a detailed investigation of optical spectra of the UV-irradiated $RbNO_3$ and $CsNO_3$ crystals.

2. Experimental

Alkali nitrate crystals were grown by slow evaporation of saturated aqueous solutions. The nitrates used were a.r. grade (three times crystallized from redistilled water before use). A typical dimension of the samples was 1 cm × 0.5 cm and their thickness varied from 0.0040 to 0.2000 cm.

The procedure for the chemical analysis of nitrite and peroxynitrite was described earlier [13,14].

The samples were irradiated at room temperature with a low-pressure mercury lamp, whose 87% irradiation energy corresponds to 253.7 nm. The light was not focused. The irradiated samples before use were stored at room temperature for 30 min. The experiments were made on polished crystals cut parallel to growth sides of the $RbNO_3$ and $CsNO_3$ crystals.

The photo-bleaching was carried out with an intermediate-pressure mercury lamp, whose light (<310 nm) is completely absorbed by a glass filter. The irradiation of the samples by a low-pressure mercury lamp passed through the glass filter does not result in the photo-bleaching of UV photo-induced absorption after the exposition.

The thermal annealing of UV-photolysed crystals was carried out in the thermostat at 70 and 90 °C for $RbNO_3$ and $CsNO_3$ crystals, respectively (the accuracy was ±1 °C). The nitrite formation in non-irradiated crystals was not observed at this temperature.

The method for the overlapping optical spectra resolution was described earlier [15]. The optical absorption in $RbNO_3$ and $CsNO_3$ crystals is of an isotropic character. To increase the reliability of the data, three to five crystals of each alkali nitrate were studied.

3. Experimental results

The evolution of the absorption spectrum of the starting $CsNO_3$ crystal with thickness 0.013 cm to the intermediate photo-products is shown in Fig. 1 (the absorption spectra of $RbNO_3$ crystals are almost the same). Photo-induced absorption spectra of $RbNO_3$ and $CsNO_3$ crystals exposed for 30 and 25 min, respectively, are shown in Figs. 2 and 3. The optical absorption data given in Figs. 2–6 corresponded to the data on total absorption of photolysing light by the samples.

The dependence of the photo-induced absorption accumulation versus the photolysis time is linear like peroxynitrite accumulation. The optical spectra are similar to the optical spectrum of *cis*-KOONO registered for UV-irradiated KNO_3 (193 nm) in solid argon [16]. The asymmetric shape of the spectra allows us to assume that they consist of a few bands. The analysis of optical spectra was made on the assumptions that they consist of either two or three bands. In terms of the first assumption, the band maxima for $CsNO_3$ are 355 nm and 317 nm with half-widths 5200 and 5100 cm^{-1}, respectively. The analysis of the optical spectra made on the assumption that they consist of three bands is given in Figs. 2 and 3. The data are summarized in Table 1.

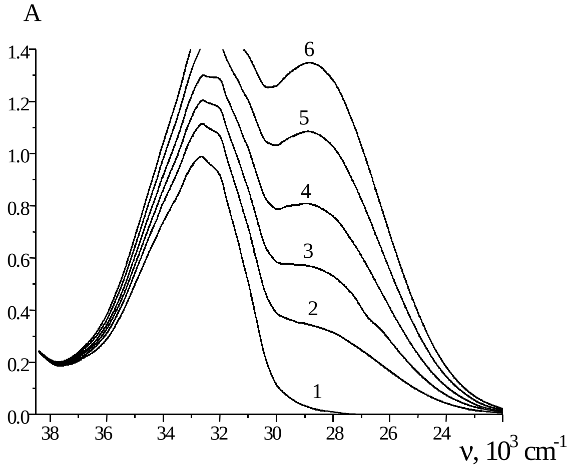

Fig. 1. Absorption spectra of UV-irradiated $CsNO_3$ crystal with thickness 0.013 cm (curves 1–6: 0, 5, 10, 15, 20 and 25 min of photolysis respectively).

The results obtained enable us to describe the data in Figs. 2 and 3 rather accurately. A maximum deviation of

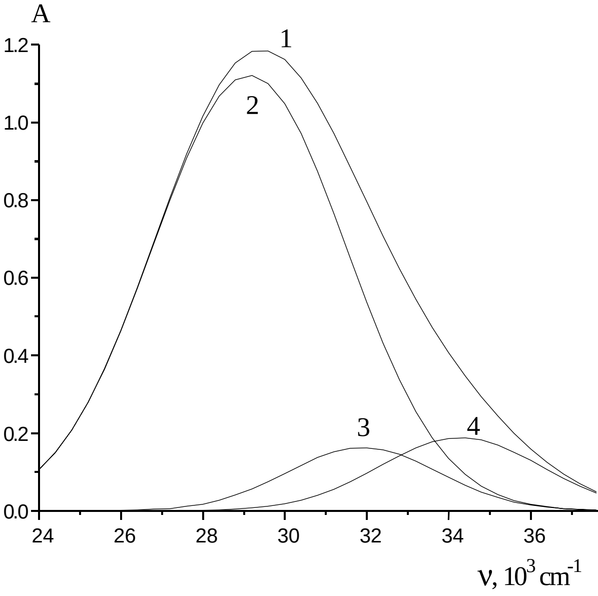

Fig. 2. Optical spectrum of the UV-irradiated $RbNO_3$ crystal after 30 min exposure (curve 1) and its analysis (curves 2–4).

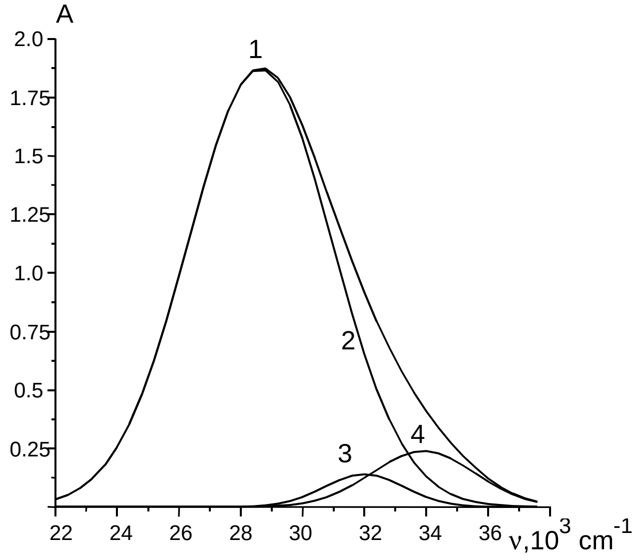

Fig. 3. Optical spectrum of the UV-irradiated $CsNO_3$ crystal after 25 min exposure (curve 1) and its analysis (curves 2–4).

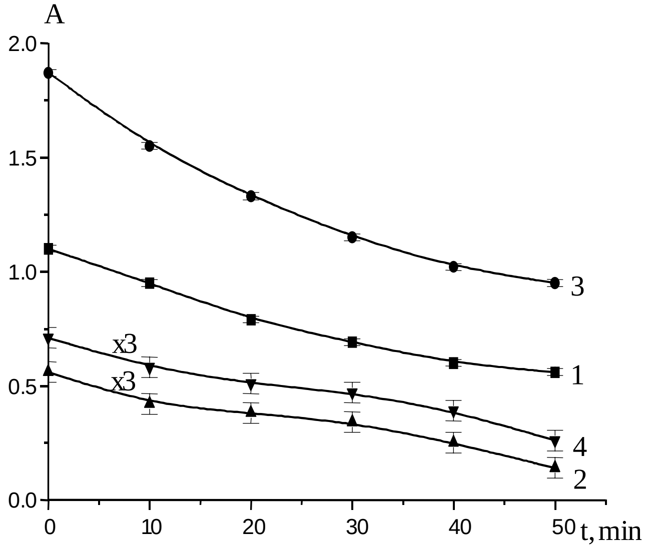

Fig. 4. Photo-bleaching of photo-induced bands in $RbNO_3$ (curves 1 and 2) and $CsNO_3$ (curves 3 and 4): (curves 1 and 3) low-energy and (curves 2 and 4) high-energy bands.

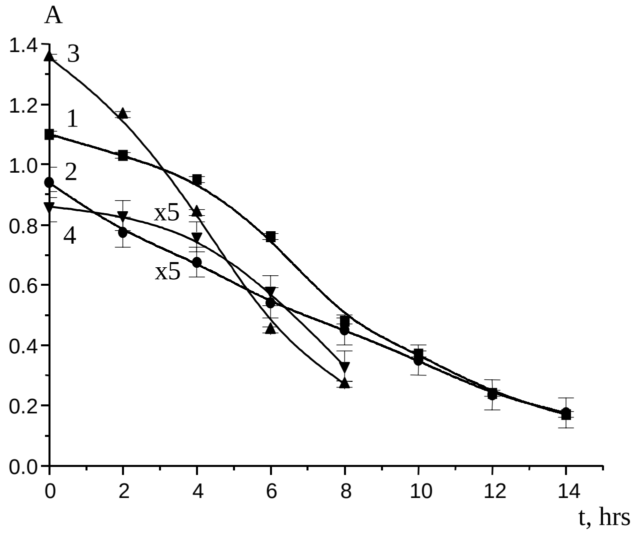

Fig. 5. Thermal annealing of photo-induced bands in $RbNO_3$ (curves 1 and 2) and $CsNO_3$ (curves 3 and 4): (curves 1 and 3) low-energy and (curves 2 and 4) high-energy bands.

theoretical values of optical density from experimental ones, $A_T - A_{exp} = \Delta A$, for both two and three bands does not exceed ± 0.01.

However, the results given below cannot be described by means of the optical spectra consisting of two bands because the deviation of theoretical values from experimental ones in high-energy region increases with the time of photo-bleaching and thermal annealing up to $\Delta A > 0.05$. In the case of the spectra consisting of three bands, the deviation does not depend on either photo-bleaching or thermal annealing. Therefore, it can be assumed that the optical spectra in UV-irradiated $RbNO_3$ and $CsNO_3$ crystals consist of three bands.

The change of intensities of the first low-energy band and of the high-energy band under photo-bleaching ($\lambda > 310$ nm) of the photo-induced bands in $CsNO_3$ and $RbNO_3$ crystals is shown in Fig. 4. The behavior of these two low-energy bands was the same under thermal annealing and photo-bleaching.

Under bleaching, the decay of the first low-energy band (hereinafter, referred to as the low-energy band) for the given exposition time can be described with the first-order kinetics. It is quite evident, because the decay of peroxynitrite described with

Table 1
Parameters of absorption bands in UV-irradiated $RbNO_3$ and $CsNO_3$ crystals[a]

Matrix	First low-energy band		Second low-energy band		High-energy band	
	λ_{max} (nm)	$H_{1/2}$ (cm^{-1})	λ_{max} (nm)	$H_{1/2}$ (cm^{-1})	λ_{max} (nm)	$H_{1/2}$ (cm^{-1})
$RbNO_3$	343	5550	313	4350	292	4650
$CsNO_3$	349	5450	313	3100	295	3950

[a] λ_{max}: position of the band maximum; and $H_{1/2}$: half-width of the band.

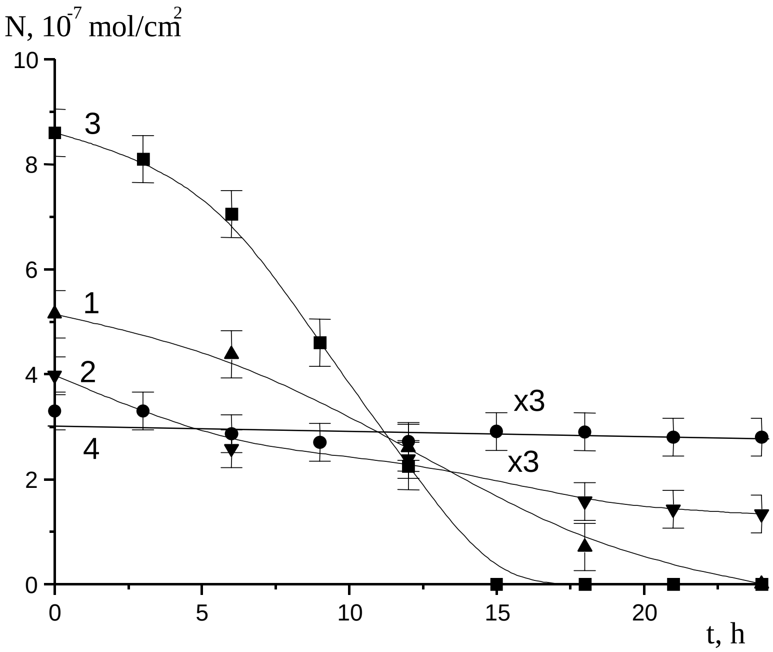

Fig. 6. Thermal annealing of photo-decomposition products determined in $RbNO_3$ (curves 1 and 2) and $CsNO_3$ (curves 3 and 4) by chemical analysis: (curves 1 and 3) peroxynitrite and (curves 2 and 4) nitrite.

(i) the second-order kinetics in solids does not occur;
(ii) the zero-order kinetics occurring in each infinitely small layer means the decrease of peroxynitrite content in the sample fits rather the first-order kinetics.

These data are in good agreement with the data [9] on the bleaching of peroxynitrite in the UV-irradiated KNO_3 obtained with chemical analysis. The kinetics of the bleaching of the high-energy band is of a more complex behavior.

The change of intensities of the low-energy band and of the high-energy band under thermal annealing is shown in Fig. 5. As seen, the annealing of the low- and high-energy bands is described by different kinetics. The content of nitrite and peroxynitrite in the UV-irradiated $RbNO_3$ and $CsNO_3$ crystals after annealing, determined by the chemical analysis, is given in Fig. 6. Peroxynitrite in the annealed samples is not observed after 15 h of annealing. The content of nitrite in annealed $RbNO_3$ within 15 h was twice as less than in untreated samples, it remaining unchangeable in $CsNO_3$.

The comparison of the data on the photo and thermal stability of the absorption bands in UV-irradiated $CsNO_3$ and $RbNO_3$ crystals with the data of chemical analysis on the decay of peroxynitrite shows that they are brought about by two different products, one of which—peroxynitrite—accounts for the two low-energy bands.

Such diamagnetic products of the nitrate aqueous solutions exposed with 253.7 nm as the peroxynitrite ion and the nitrite ion and supposedly $O_2NO_2^-$ and the complex $[NO_2^- \cdots O]$ [17] can be formed while paramagnetic products of UV-irradiated alkali nitrate crystals cannot. The absorption spectra of the peroxynitric acid is in fact a broad band with its maximum in the region shorter than 200 nm [18].

In aqueous solution, the band at 287 nm due to nitrite corresponds to the $n\pi^*$ forbidden transition (symmetry of NO_2^- is C_{2v} and its molar absorptivity is $9\,M^{-1}\,cm^{-1}$ [19]). As seen from Table 1, the positions of the maxima of the above band and the high-energy band coincide. Since other products of the decomposition of crystalline alkali nitrates under UV-photolysis in this region do not absorb light, the high-energy band can be stated to be due to nitrite. However, if it were the case molar absorptivity of nitrite must be two orders of magnitude higher. Thus, the coupled-exchange complex $[NO_2^- \cdots O]$ can be assumed to be formed under photolysis. The $n\pi^*$ transition in the nitrite ion in this complex is allowed because of the deformation of the nitrite-ion up to C_s symmetry. However, the observed band can be due to the charge transfer from one component of the complex to the other.

The complex $[NO_2^- \cdots O]$ in solid nitrates is stable if the diffusion of atomic oxygen does not take place. Johnson [20] stated that since radiation yields of nitrite in solid nitrates do not depend on the absorbed dose rate (10^{15} to 10^{20} eV g^{-1} c^{-1}), the reaction $O + O = O_2$ can be ignored for the radiolysis of nitrates. Since the concentration of nitrite (consequently, of atomic oxygen) formed under the photolysis of solid nitrates does not exceed the one under radiolysis, it can be stated that the reactions of atomic oxygen with photo-products can be neglected. Thus, the above assumption that atomic oxygen is located near the nitrite ion is justified.

The detection of the complex in solids would be possible due to the luminescence of exposed samples. However, direct excitation of atomic oxygen in this energy region is impossible while the transfer of the energy from the nitrate ion to atomic oxygen can be neglected because the peroxynitrite ions and the nitrite ions are effective excitation quenchers [21].

4. Discussion

The peroxynitrite ion is formed from the singlet high-energy excited state of the nitrate ion $(NO_3{}^-)^*$ $(\pi\pi^*)$ [22].

$$^1(NO_3{}^-)^*(\pi\pi^*) \rightarrow ONOO^- \qquad (1)$$

The non-linear behavior of the kinetics of peroxynitrite accumulation [5–7] shows that its bleaching by means of low-energy excited states of the nitrate ions $(NO_3{}^-)^*$ $(n\pi^*)$ formed from initial excited states $^1(NO_3{}^-)^*$ $(\pi\pi^*)$ occurs under photolysis. This assumption can be supported by the following:

(i) photo-decomposition products of alkali nitrate crystals do not absorb photolysing light (Figs. 2 and 3);
(ii) peroxynitrite is stable at room temperature in solid state;
(iii) photo-bleaching of peroxynitrite occurs under UV irradiation at ~300 nm (the quantum energy is equal to the $(n\pi^*)$ excited states of the nitrate ion). The low-intensity filtered light of the low-pressure mercury lamp fails to produce the photo-bleaching of peroxynitrite.

The first stage of bleaching results in the formation of the triplet or singlet excited states of the peroxynitrite ion.

$$^{1,3}(NO_3{}^-)^*(n\pi^*) + ONOO^- \rightarrow {}^{1,3}(ONOO^-)^* + NO_3{}^- \qquad (2)$$

The formation of the coupled-exchange complex $[NO_2{}^- \cdots O]$, when the exposition time corresponds to the initial linear accumulation of peroxynitrite, takes place only from the triplet excited nitrate ions $(n\pi^*)$.

$$^3(NO_3{}^-)^*(n\pi^*) \rightarrow [NO_2{}^- \cdots O] \qquad (3)$$

With the exposition time increasing, it can also be formed from the triplet excited state of the peroxynitrite ion

$$^3(ONOO^-)^* \rightarrow [NO_2{}^- \cdots O] \qquad (4)$$

This process must be accompanied by the formation of the additional content of the complex, which can be graphically represented by the deviation from the linear region on the accumulation curve of the high-energy band. Unfortunately, we failed to obtained optical spectra ($A > 1.4$) corresponding to the required exposition time.

The photolysis (>300 nm) of UV pre-irradiated samples results in singlet excited states of the peroxynitrte ions, hence the reaction (4) is decisive only under UV irradiation (253.7 nm).

The singlet excited state of peroxynitrite ion can either undergo isomerization [5]

$$^1(ONOO^-)^* \rightarrow NO_3{}^- \qquad (5)$$

or change into the ground state

$$(ONOO^-)^* \rightarrow ONOO^- \qquad (6)$$

On the basis of the data on the photo-bleaching of the photo-induced high-energy band, it follows that the decay of the coupled-exchange complex during photolysis must result from the low-energy excited states of nitrate ions $(NO_3{}^-)^*$ $(n\pi^*)$ because it absorbs neither the photolysing light nor the light >310 nm.

$$(NO_3{}^-)^*(n\pi^*) + [NO_2{}^- \cdots O] \rightarrow [NO_2{}^- \cdots O]^* + NO_3{}^- \qquad (7)$$

This assumption can be confirmed by the shape of the kinetic curve of the photo-bleaching of the high-energy band as the decay of the complex increases depending on the duration of bleaching, i.e. when the quantity of energy absorbed by peroxynitrite is less than that absorbed by the host matrix. The products of the bleaching of the complex can be both the nitrite ion and the nitrate ion but not the peroxynitrite ion

$$[NO_2{}^- \cdots O]^* \rightarrow NO_3{}^- \qquad (8)$$

$$[NO_2{}^- \cdots O]^* + NO_3{}^- \rightarrow 2NO_2{}^- + O_2 \qquad (9)$$

Therefore, it is necessary to develop the mechanism for the formation of the peroxynitrite ion. Its formation from the nitrate ion must proceed via an intermediate which includes both oxygen and nitrogroup fragments as constituents of the complex $[NO^\bullet \cdots O_2]^-$.

$$^1(NO_3{}^-)^*(\pi\pi^*) \rightarrow [NO^\bullet \cdots O_2]^- \qquad (10)$$

This is supported by the fact that the $O_2{}^{\bullet-}$ or $O^{\bullet-}$ centres are not formed since the ESR spectra for UV-irradiated alkali nitrate crystals at 254 nm are not registered [9]. The complex $[NO^\bullet \cdots O_2]^-$ is not stabile in alkali nitrate crystals and is immediately converted into the peroxynitrite ion [23]

$$[NO^\bullet \cdots O_2]^- \rightarrow ONOO^- \qquad (11)$$

Based on the contents of the complex $[NO_2{}^- \cdots O]$, nitrite and peroxynitrite (Figs. 5 and 6) before and after thermal annealing, it follows that the decay of the complex $[NO_2{}^- \cdots O]$ results in the nitrate ion or the nitrite ion while the decay of the peroxynitrite ion results in the nitrate ion only.

When dissolving UV-irradiated alkali nitrate crystals, the complex $[NO_2{}^- \cdots O]$ is changed into the nitrate or nitrite ions, but the peroxynitrite ion, either into the complex $[NO_2{}^- \cdots O]$ or the nitrate ion or nitrite ion depending on both the concentration of peroxynitrite and pH [24].

The kinetic analysis of the experimental data has not been carried out by the present authors because it is experimentally impossible to estimate the content of the complex $[NO_2^- \cdots O]$ in UV-irradiated samples.

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